Studies into the formation of PBDEs and PBDD/Fs in the iron ore sintering process

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Abstract: Polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and furans (PBDD/Fs) were detected in stack emissions from UK sinter plants. The sum of 36 PBDE congeners was measured at a mean concentration of 295 ng/Nm3 with a standard deviation of 96 ng/Nm3. The mean PBDD/F concentrations were 0.14 ng WHO-TEQ/m3 (range = 0.03 - 0.39). PBDD/F emission concentrations were approximately ten times lower than their PCDD/F homologues. To understand the possible formation mechanisms of brominated organic species in iron ore sintering, both full-scale and laboratory experiments using an experimental sintering process were carried out. A complete PBDE mass balance was undertaken for a full scale sinter plant showing that PBDEs were already present in the raw materials such as iron ores and coke breeze and that a significant proportion of the PBDE inputs were actually destroyed during the process. A number of controlled experiments were conducted using a laboratory-scale sintering apparatus (sinter pot). These were designed to investigate: (a) mass balance of PBDEs during sintering, (b) the relationship between the availability of bromide (as KBr) and PBDE emissions, and (c) the influence of the availability of both bromide and PBDEs on PBDD/F formation. As observed in the full scale plant, the PBDEs already present in the raw materials were mostly destroyed during the process (79-96%) for all sinter pot experiments. Increasing amounts of KBr in the raw sinter mix did not result in a significant increase in PBDE formation suggesting that there was no PBDE formation in sintering via de novo synthesis. No relationship was observed between PBDE inputs and PBDD/F emissions indicating that PBDEs did not act as precursors for PBDD/Fs formation. Finally, PBDD/F formation was enhanced substantially with increasing amounts of KBr suggesting that their formation mechanism was similar to that of PCDD/Fs via de novo synthesis.

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Cover Letter

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R.E. Alcock
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Dear Editor-in-chief

We submit this manuscript entitled "Studies into the Formation of PBDEs and PBDD/Fs in the Iron Ore Sintering Process" by Daniel Drage, Eric Aries and Stuart Harrad to be considered for publication as a research paper for Environment International.

The manuscript describes the movement of PBDEs (and output of PBDD/Fs) through the iron ore sintering process during integrated steel manufactur – both on a commercial and laboratory scale. To the knowledge of all the authors this is the first study that has examined the raw material inputs into the sintering process for PBDEs to examine whether *de novo* formation of PBDEs and PBDD/Fs occurs, as well as the potential conversion of PBDEs to PBDD/Fs during this process. We believe the findings of this article are ideal for this journal - providing the most complete dataset on the movement of PBDEs and PBDD/Fs through the iron ore sintering process – a key anthropogenic activity conducted globally and known to be a source of direct release to the environment of persistent organic pollutants.

This is an original manuscript that has not been published before and is not currently being considered for publication elsewhere – although the initial findings were presented at BFR 2013 – the Sixth International Symposium On Flame Retardants in April 2013.

We confirm that the manuscript has been read and approved by all named authors.

We hope that you find the manuscript suitable for publication and look forward to hearing from you.

Sincerely,

Dr. Daniel Drage
Doctoral Researcher
University of Birmingham

Studies into the Formation of PBDEs and PBDD/Fs in the Iron Ore Sintering Process

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ABSTRACT. Polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) were detected in stack emissions from UK sinter plants. The sum of 36 PBDE congeners was measured at a mean concentration of 295 ng/Nm^3 with a standard deviation of 96 ng/Nm^3. The mean PBDD/F concentrations were 0.14 ng WHO-TEQ/m^3 (range = 0.03 - 0.39). PBDD/F emission concentrations were approximately ten times lower than their PCDD/F homologues. To understand the possible formation mechanisms of brominated organic species in iron ore sintering, both full-scale and laboratory experiments using an experimental sintering process were carried out. A complete PBDE mass balance was undertaken for a full scale sinter plant showing that PBDEs were already present in the raw materials such as iron ores and coke breeze and that a significant proportion of the PBDE inputs were actually destroyed during the process. A number of controlled experiments were conducted using a laboratory-scale sintering apparatus (sinter pot). These were designed to investigate: (a) mass balance of PBDEs during sintering, (b) the relationship between the availability of bromide (as KBr) and PBDE emissions, and (c) the influence of the availability of both bromide and PBDEs on PBDD/F formation. As observed in the full scale plant, the PBDEs already present in the raw materials were mostly destroyed during the process (79-96%) for all sinter pot experiments. Increasing amounts of KBr in the raw sinter mix did not result in a significant increase in PBDE formation suggesting that there was no PBDE formation in sintering via *de novo* synthesis. No relationship was observed between PBDE inputs and PBDD/F emissions indicating that PBDEs did not act as precursors for PBDD/Fs formation. Finally, PBDD/F formation was enhanced substantially with increasing amounts of KBr suggesting that their formation mechanism was similar to that of PCDD/Fs via *de novo* synthesis.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been one of the most commonly used brominated flame retardants (BFRs) with a global demand of 67,000 tonnes in 2001 – the last year for which production figures were available (Bromine Science and Environmental Forum (BSEF), 2003). They have a wide range of consumer applications and uses, such as in foam-upholstered furniture, and high impact polystyrene (HIPS) casings for electrical goods, (Da'Silva et al., 2004; Bromine Science Environmental Forum, 2007). Such extensive and myriad uses have led to substantial contamination of both indoor and outdoor environments, leading to exposure of both humans and wildlife (Darnerud, 2003; Montaño et al., 2013). Such contamination, coupled with evidence of potential adverse human health effects have led to bans and restrictions on the manufacture and new use of PBDEs in various jurisdictions around the world – the most high profile of which was the listing of the Penta- and Octa-BDE commercial formulations under the Stockholm Convention on Persistent Organic Pollutants (Stockholm Convention, 2009). Although emissions of PBDEs associated with the remaining reservoir of treated products both in-use and entering the waste stream are likely to continue for the foreseeable future (Harrad and Diamond, 2006); any other sources of PBDEs are likely to assume progressively greater importance in future as the legacy of their commercial use diminishes.

An additional source of concern about PBDEs is their possible role as precursors for the formation of polybrominated dibenzo-*p*-dioxins and furans (PBDD/Fs) (Buser, 1986; Wang et al., 2010b). PBDD/Fs have comparable physicochemical properties to the well-studied PCDD/Fs (Ren et al., 2009), although the comparative weakness of the C-Br bond is likely to lead to different environmental fate and behaviour to that observed for PCDD/Fs (Schecter, 2012). One of the main release pathways of PBDD/Fs is believed to be as a by-product of the use, manufacture and recycling of BFR containing goods, with PBDEs acting as precursors to PBDD/Fs in high temperature processes (Buser, 1986).

There are very few studies concerning PBDD/F emissions and exposure pathways/health effects, with a very small number of studies based on humans (Ericson Jogsten et al., 2010). The toxicity of PBDD/Fs is still relatively unknown, especially when compared to that of PCDD/Fs (Birnbaum et al., 2003). However, there is limited information on some specific congeners such as 2,3,7,8-tetrabromodibenzo-*p*-dioxin (TBDD) to which humans can be

exposed to through inhalation and ingestion (Birnbaum and Staskal, 2004), and it is known that PBDD/Fs are metabolised extremely slowly with human half-lives of approximately 5-10 years (Birnbaum et al., 2003). The overall health effects of PBDD/Fs are believed to be similar to those of PCDD/Fs, based on mammalian and amphibian experiments – lethality, wasting, thymic atrophy, teratogenesis, reproductive disturbance, chloracne, immunotoxicity, enzyme reduction, T4 vitamin A reduction, and increased hepatic porphyrins (Birnbaum et al., 2003).

Although literature is scarce with regards to the steel industry as a source of PBDEs and PBDD/Fs, there is growing evidence to suggest that it may be a source of brominated organic micro-pollutants in the environment. PBDE concentrations in ambient air within a steel complex in Korea were found to be twice those of background concentrations (Choi et al., 2008). Ferrous scrap is believed to contain PBDEs from previous uses, such as in cars and vehicles containing technical mixtures (Choi et al., 2008; Odabasi et al., 2009). The Electric Arc Furnace (EAF) process which consists mainly in recycling ferrous scrap steel products has therefore been identified as the main source of PBDEs from steelmaking activities (Odabasi et al. 2009). However, more recently, it has also been suggested that the iron ore sintering process could lead to the formation of PBDEs and PBDD/Fs (Wang et al. 2010b). For use in the blast furnaces, the iron ores are first processed in large iron ore sintering plants. In iron ore sintering, the objective is to agglomerate iron ore fines into a product designated as sinter which is composed of permeable lumps which provide the necessary permeability for blast furnace operation. The feed of the iron ore sintering process consists of a moist agglomerate of fine-grained iron ores, recycled materials, coke breeze and limestone. The feed is laid on a moving belt and coke particles in the top layer of the materials are ignited by gas burners thus creating a combustion front. Air is drawn downwards through the sinter bed into a series of wind boxes beneath the strand. The process is carried out by wet mixing the ore with 3-4 % weight of coke breeze and the other additives and spreading the mixture on a base moving at 2-3 m/min, typically 2-4 m wide to a depth of 0.4-0.5 m. The combustion process is initiated at the top of the bed and drawn through it by an induced draught fan via a series of ducts below the bed. As the coke fines burn in the bed, the heat generated sinters the fine particles and the temperature of the bed reaches 1300-1480 °C. At the end of the strand, the sinter product falls off into a cooling system, typically a carousel.

The iron ore sintering process has been studied in detail in the past with regard to the formation of PCDD/Fs and PCBs, and was identified as the most significant source of these

compounds from steelmaking activities (Anderson and Fisher, 2002; Aries et al., 2006). In sintering, the temperature of the waste gases are about 160°C, which is well below the range of 250 - 450°C generally considered to be favourable for PCDD/F formation via *de novo* synthesis (Vogg and Stieglitz, 1986). However, it has been proposed that PCDD/F formation in iron ore sintering occurs mainly in the dry zone of the sintering bed, within the sinter bed itself, ahead of the flame front. Here temperatures can reach as high as 1100 °C but areas of 250 to 450 °C also exist for *de novo* synthesis to take place (Anderson and Fisher, 2002; Suzuki et al., 2004).

In comparison with PCBs and PCDD/Fs, there is little information on the potential formation mechanisms of PBDD/Fs and PBDEs in iron ore sintering. Accordingly, using a combination of full-scale investigations by measuring sinter stack emissions at UK sinter plants and realising a series of controlled laboratory-scale experiments, this paper investigates the hypothesis that the iron ore sintering process could be a source of PBDEs and PBDD/Fs to the environment. In so doing, it provides novel insights into the sources and possible formation pathways of these contaminants in the sintering process. In particular, we investigated the possibility that: (a) PBDEs may act as precursors to the formation of PBDD/Fs in the sintering process, (b) the sintering process may lead to the formation of PBDEs, and (c) the bromide content of the raw mix could play a major role in the formation of either PBDEs and / or PBDD/Fs during sintering. In addition, a wide range of raw material inputs (iron ores, coke breeze, revert materials from iron-making and steelmaking processes) and output materials (waste electrostatic precipitator (ESP) dusts, stack emission samples) were analysed to carry out detailed PBDE mass balances in the sintering process.

2. Sampling methods

In this study, measurement of PBDEs and PBDD/Fs were realised in a wide variety of samples collected at a sinter plant operated by Tata Steel in the UK. The sinter plant selected for this study was typical in terms of design and operation of most sinter plants currently in operation in Europe and around the world. Amongst the samples analysed, a wide range of inputs (raw materials such as iron ores, coke breeze and limestone) and output samples (sinter product, and waste dusts collected from the electrostatic precipitators - ESP dusts) were collected. In addition, a series of stationary source emission samples were collected from the sinter stack to measure waste gas emissions of PBDEs and PBDD/Fs. These samples enabled the calculation of detailed mass balances for PBDEs in iron ore sintering.

2.1 Sampling of solid samples

Raw material samples were collected at various stages of the sintering process and stored in glass amber jars. These samples consisted of iron ores (n = 26), revert materials (i.e. reverts) – such as waste dusts from the blast furnaces or steelmaking processes (n = 20), fluxes such as limestone (n = 5), and fuels such as coke breeze (n = 3). For mass balance determinations, input and output samples collected during the processing of the same bed of materials were analysed. These included raw sinter mix (RSM) samples (n=6), composed of a blend of iron ores, reverts, fluxes and fuels and output materials including the sinter product (n = 6), and ESP dusts (n = 8). All the raw materials – except for the sinter product – were collected as coarse dusts and were transferred to amber jars ready for extraction and clean-up. The sinter product samples were crushed into dusts using a Tema T750k laboratory disc mill prior to extraction for PBDE analysis.

2.2 Stack emission sampling

In total, twelve sinter plant stack emission samples were analysed for PBDEs and fifteen were analysed for PBDD/Fs. These were taken by MCERTs accredited sampling teams at Tata Steel using the European Air Method in accordance with British and European standards (BS EN 1948). Briefly, emission samples were taken isokinetically from the sinter plant stack via a 3 m long heated (>120°C) titanium or quartz glass-lined sampling probe. Particulate matter was collected on a glass fibre filter, contained in a heated filter box (>120°C), whilst vapour phase PBDD/Fs and PBDEs were trapped on an appropriately spiked XAD-2 resin contained in a water-cooled glass vessel. After sampling, the probe liner was washed successively with acetone, dichloromethane, and toluene and the resulting washings were collected, combined, and retained for analysis with the rest of the sampling media.

2.3 Sinter Pot Sampling

The sinter pot is a well-established experimental technique for studying the effects of process factors on sinter quality and productivity, but in recent years the technique has been extended to the study of factors governing the formation and emission of organic pollutants in the sintering process (Ooi et al., 2008). Conventional sinter pots have a charge capacity of around 80 – 100 kg per run, but a laboratory-scale unit - shown schematically in Fig. 1 - was used in the present study. The sinter pot has a capacity of 1.0 kg and the bed diameter and height are 100 and 150 mm, respectively. The RSM is charged as micro-pellets onto a layer of hearth

material, approximately 25 mm thick, consisting of sinter cake pieces supported on a 3 mm thick stainless steel mesh. The inner walls of the sinter pot are lined with fine ores to reduce adhesion of the sinter product to the inner wall of the pot and to fill fissures between the inner wall and sintered material ensuring constant airflow through the bed during sintering. The SP is connected to a suction fan via a windbox attached to base of the pot. Thermocouples were installed at various depths through the sinter bed and in the windbox to record the progression of the heat front through the sinter bed and off-gas temperature. The RSM was ignited by adding a fixed amount of coke, ca. 20 g, to the top of the raw sinter material and heating it with an oxy-propane burner for 30 s. A fixed sintering air velocity of 0.44 m/s, which corresponds to a total gas flow of 1.0 m^3 for a typical pot firing operation, was maintained throughout the sintering process. Air flow measurements were made in the off gas passage where the hot exhaust gas has been cooled.

In each experiment, approximately 1 kg of RSM was prepared for sintering in the same way as in the full-scale production process. The RSM was sintered and a total emission sample (both particulate and gas phase combined) collected via a PUF plug (6 cm i.d. x 7.6 cm length), Supelco, UK). The outer layer of the remaining sinter product was "chiselled" with samples taken from the centre and crushed using a Tema T750 k laboratory disc mill. This allowed for a total mass balance of the sintering process to be calculated. In total, five different SP experiments were conducted as described in Table 1. The first experiment was carried out on a standard RSM designated as a base case. In experiment 2, bromide (as KBr) was added to the RSM at an addition rate of 74.5 mg/kg. In experiment 3, a higher addition rate of KBr was used (ca. 224 mg/kg). In experiment 4, significant amounts (ca. 50 μg/kg) of two PBDE technical mixtures were added to the raw sinter mix to study the potential conversion of PBDEs into PBDD/Fs during sintering. The technical mixtures used were DE-71 and DE-83, Penta- and Deca-BDE formulations respectively (Cambridge Isotope Laboratories (CIL), Andover, MA, USA). Finally in experiment 5, both KBr and the technical mixtures were added to the RSM. Each experiment was conducted in duplicate.

3. Sample preparation and analytical methods

3.1 *Solid Samples (PBDEs)*

All the solid samples were analysed at the University of Birmingham. They were spiked with known quantities of internal (or surrogate) standards (IS) ($^{13}C_{12}$-BDEs-47, -99, -153, Wellington Laboratories Inc., Ontario, Canada) prior to pressurised liquid extraction (PLE)

using an ASE 350 (Dionex, California, USA). The extract was concentrated to 0.5 mL under a gentle stream of nitrogen using a Zymark Turbovap® II concentration workstation (Hopkinton, MA, USA) reconstituted into hexane and washed with <95% concentrated sulfuric acid (Sigma Aldrich, UK) in a 10 mL conical test tube. The top (hexane) layer and three subsequent washings were collected and passed through a column containing florisil (60-100 mesh, Sigma Aldrich, UK) and 1 g sodium sulfate (Sigma Aldric, UK). 20 mL hexane was washed through the column, the complete eluate was collected in 50 mL Turbovap® tubes and concentrated under nitrogen to near dryness. Known amounts of recovery determination standard were added ($^{13}C_{12}$-BDE 100, Wellington Laboratories Inc., Ontario, Canada) and the sample was made up to 50 µL in methanol.

3.2 *Stack Emission Samples (PBDD/Fs / PCDD/Fs)*

Stack emission samples were analysed both for their PBDD/F and PCDD/F concentrations. For PCDD/Fs, samples were analysed following the CEN-1948-4 European Standard for the determination of the mass concentration of PCDD/PCDF in stationary source emission samples. For PBDD/Fs, emission samples were spiked with known quantities of IS ($^{13}C_{12}$-1,2,3,7,8-PeBDF, $^{13}C_{12}$-2,3,7,8-TeBDF, $^{13}C_{12}$-2,3,7,8-TBDD, $^{13}C_{12}$-1,2,3,7,8-PeBDD, $^{13}C_{12}$-1,2,3,7,8,9-HxBDD) prior to PLE using an ASE 200 (Dionex, California, USA). The extracts were concentrated using nitrogen and a water bath to ca. 0.5-1.0 mL before being passed sequentially through a Supelco Dioxin Prep System Column of 15 mm internal diameter and 35 cm length containing 7 layers of treated silica gels that oxidise, reduce, and separate polar interferences. The extract was subsequently cleaned up by using an activated Florisil column (containing 1 g pre-extracted Florisil (Sigma Aldrich) to separate PCBs from PBDD/Fs and PCDD/Fs. The eluate was then transferred along with washings into a Zymark Turbovap (II) concentration workstation (Zymark, Warrington, UK) for concentration under a stream of nitrogen. Nonane and a recovery determination (or syringe) standard ($^{13}C_{12}$-2,3,4,7,8-PeBDF) were added up to a volume of 50 µl prior to analysis.

3.2 *Stack Emission Samples (PBDEs)*

The stack emission sample analysed for PBDEs were subjected to almost identical extraction and clean-up procedures as those detailed above for PBDD/Fs, except that the clean-up procedure was carried out on a multi-layered silica column different from the commercially available Supelco Dioxin Prep System columns. For PBDEs, a multi-layered silica column containing several layers of activated silica gel (6 g), basic silica gel (6 g) and acidic silica gel

(30 g) was used. Prior to extraction, samples were spiked with known quantities of IS ($^{13}C_{12}$-BDE-4, $^{13}C_{12}$-BDE-15, $^{13}C_{12}$-BDE-28, $^{13}C_{12}$-BDE-47, $^{13}C_{12}$-BDE-100, $^{13}C_{12}$-BDE-99, $^{13}C_{12}$-BDE-118, $^{13}C_{12}$-BDE-153, and $^{13}C_{12}$-BDE-183). After Florisil clean-up, the PBDE fraction (identical to the PCB fraction) was transferred along with washings into a Zymark Turbovap (II) concentration workstation for concentration under a stream of nitrogen. Nonane and recovery standards ($^{13}C_{12}$-BDE-77 and $^{13}C_{12}$-BDE-126) were added up to a volume of 50 µL prior to analysis.

3.4 *Sinter Pot Emission Samples*

Sinter pot samples were extracted using toluene with an ASE 200. A 10% fraction of the crude extract was retained for PBDE clean-up and analysis at the University of Birmingham following the analytical procedure described in Section 1.3.1. The remainder of the crude extract was analysed for PBDD/Fs at Tata Steel following the analytical procedures described in Section 1.3.2.

3.5 *PBDE analysis*

All the PBDE analyses for the raw materials and sinter pot samples were conducted at the University of Birmingham. All samples except for the RSM components (iron ores, reverts, fuels and fluxes) were analysed by GC/MS. GC/MS analysis was carried out on an Agilent 5975 MS coupled with an Agilent 6850 GC with an Agilent DB-5ms column (30m x 0.25 i.d. x 0.25 µm film thickness). 1 µL of extract was injected in splitless mode at 250 °C. The initial oven temperature was 70 °C which was held for 2 minutes, then increased by 20 °C/min to 270 °C and held at for 53 minutes. The MS was run in EI selected ion monitoring mode (ionization voltage = 70 eV; ion source temperature = 250 °C**)** and monitored for 6 ions (BDE -47: 485.8, 483.9; BDEs -85, -99 and -100: 403.9, 405.9; BDEs -153 and -154: 483.9, 481.9). RSM components were analysed by LC-APPI-MS/MS for BDEs -47, -85, -99, -100, -153 and -154 (Abdallah et al., 2009). Blanks of PLE pre-extracted diatomaceous earth were analysed and found not to contain target PBDEs. Recoveries of internal standards ranged from 37-149% with an average of 95% across all samples. Analytical precision was assessed by replicate analysis (n=12) of SRM 2585 (NIST) and achieved values close to the certified figures. Method detection limits were 0.36-1.4 ng/g for GC/MS and 8.8-21 ng/g for LC-APPI-MS/MS.

With regard to the stack emission samples, analyses were carried out at Tata Steel by High Resolution Gas Chromatography – High Resolution Mass Spectrometry. (HRGC – HRMS) using an Agilent 5973 GC coupled to an Autospec Ultima HRMS (Waters, Manchester, UK). Analysis was carried out using a DB-XLB capillary column of 30 m length, 0.25 mm i.d. and 0.1 µm film thickness. 1 µL of extract was injected in splitless mode with an injector temperature of 280ºC. The oven temperature programme started at 100ºC for 1 min, then ramped at 20ºC/min to 310ºC and held for 15 min. The HRMS was operated at 10000 resolution in the positive ion mode at 34eV energy with perfluorokerosene as the mass range calibrant. A 7-function SIM experiment was set up to detect two isotope ion masses for each of the mono- through to hepta-BDEs. A five-point calibration curve was generated using the calibration solutions EO-5104 (CS2 to CS6) from Cambridge Isotope Laboratories (LGC Promochem, UK). Response factors were calculated for each PBDE congener relative to available $^{13}C_{12}$-labelled homologue standards. Recoveries for PBDEs 28, 47, 99, 100, 153, 154, and 183 were determined against $^{13}C_{12}$- labelled PBDE 77 and 126. In total, 36 PBDE congeners were analysed using this method.

3.6 PBDD/F analysis

Analysis of PBDD/Fs was carried out at Swinden Technology Centre (Tata Steel, Moorgate, Rotherham, UK) via HRGC/HRMS using an Autospec Ultima (Waters). Samples were injected into a GC equipped with an Agilent DB-5MS column 30 m (length) x 0.25 mm (internal diameter) x 0.1 µm (film thickness). Helium was used as the carrier gas with a constant flow of 1.0 mL/min. The inlet was run in splitless mode. Initial temperature was 140 °C for 1 minute. The temperature was then increased to 200 °C at a rate of 20 °C/min and held for 6 minutes, then increased to 280 °C at 5 °C/min and held for 4 minutes. Samples were monitored for 9 PBDD/F compounds, namely: 2,3,78-TBDF; 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF, 2,3,7,8-TBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8-HxBDD, 1,2,3,6,7,8-HxBDD, and 1,2,3,7,8,9-HxBDD. Using this temperature programme, 1,2,3,4,7,8-HxBDD and 1,2,3,6,7,8-HxBDD co-eluted, so their concentrations are reported together in this study.

4 Results and Discussion

4.1 Stack emission results for PCDD/Fs and PBDD/Fs

A series of fifteen stack emission samples were collected from two UK sinter plants operated by Tata Steel and were analysed for their PCDD/F and PBDD/F concentrations. Table 2 summarises the mean and range of concentrations observed for the PBDD/F congeners detected in this study. In addition, Fig. 2 compares the range of PCDD/F and PBDD/F emissions at both sinter plants. For this analysis, PBDD/F emission concentrations were converted to WHO-TEQ concentrations by assuming that PBDD/F and PCDD/F have identical toxic equivalency factors (WHO-TEFs), as recommended by the World Health Organisation (Van den Berg et al. 2013). As may be seen from Fig. 2 and Table 2, PBDD/Fs were detected in the emission samples from both sinter plants within the range 0.03 - 0.39 ng WHO-TEQ/m^3. There were no significant differences between the range and mean PBDD/F concentrations observed at the two sinter plants. When analysing the individual PBDD/F congener concentrations (Table 2), PBDFs were found at significantly higher concentrations than PBDDs (ca. 10-fold). For instance, the mean ΣPBDF concentration at Sinter Plant B was 0.66 ng/Nm^3 whereas the mean ΣPBDD concentration was only 0.05 ng/Nm^3. On average, PBDFs contributed over 93% to the total PBDD/F concentration in all the stack emission samples collected. The most abundant congeners were 2,3,7,8-TeBDF, 1,2,3,7,8 PeBDF and 2,3,4,7,8-PeBDF contributing on average ca. 32%, 31% and 28% of the total PBDD/F concentrations, respectively. Du et al. (2010a) reported PBDD/F emission concentrations from a sinter plant in China to also show a marked predominance of PBDFs over PBDDs, with PBDFs contributing over 75% of the total PBDD/F concentrations. The highest PBDD/F WHO-TEQ concentration reported by Du et al was 1.1 ng WHO-TEQ/Nm^3, which exceeded that reported in our study (ca. 0.39 ng WHO-TEQ/Nm^3). In the work carried out by Du et al. (2010a), emission samples from other industrial processes (including municipal waste incineration, copper and lead smelting facilities) were also analysed for their PBDD/F emissions. The results indicated that the highest PBDD/F emissions were found at a zinc smelting plant (ca. 1.5 ng WHO-TEQ/m^3), followed by a lead smelting facility (ca. 0.7 ng WHO-TEQ/m^3) and a copper smelting plant (ca. 0.39 ng WHO-TEQ/m^3). These concentrations exceeded the PBDD/F concentrations typically determined at the iron ore sintering plants investigated in the current study. In Table 2 and Fig. 2, a comparison is made between PBDD/F emissions and the concentrations of their chlorinated homologues (PCDD/Fs). Analysis of the data showed that the magnitude of PCDD/F emissions far

exceeded those of PBDD/Fs. The mean PCDD/F emissions were typically 1.0 ng WHO-TEQ/Nm^3 at both UK sinter plants, approximately 10-fold higher than the PBDD/F concentrations (Table 1). As a result, PBDD/Fs only accounted for ca. 10% of the total WHO-TEQ emission concentrations (PBDD/Fs + PCDD/Fs). The contribution of PBDD/Fs to the overall toxicity of sinter plant emissions was therefore very similar to the contribution of the WHO-12 PCBs which have been shown to be within the range 5 – 7% in a previous study at sinter plants operated by Tata Steel (Aries et al., 2006). These results clearly showed that although PBDD/Fs were emitted from the iron ore sintering process, the magnitude of these emissions was substantially lower than that of PCDD/Fs. It is believed that PBDD/F emissions are much lower than PCDD/F emissions because the soluble bromide concentrations in the raw sinter mix are substantially lower (typically below 5 mg/kg) than soluble chloride concentrations (typically within the range 20 to 80 mg/kg).

4.2 *Stack emission results for PBDEs*

A series of twelve stack emission samples were obtained at a UK Sinter Plant operated by Tata Steel and analysed for their PBDE concentrations. In total, 36 PBDE congeners were analysed by HRGC – HRMS. The emission concentrations and congener profiles for the compounds analysed are depicted in Fig. 3. In addition, Table 3 summarises the emissions concentrations of the most predominant congeners identified in this study. The results showed that the mean PBDE emission concentrations (sum of 36 PBDE congeners) was 295 ng/Nm^3, with a standard deviation of 96 ng/Nm^3. A very characteristic emission profile was obtained with a clear predominance of BDE-99 (average = 109 ng/Nm^3) and BDE-47 (average = 75 ng/Nm^3), followed by BDE-71 (and/or BDE-49 since both compounds co-eluted in our study) with an average concentration of 32 ng/Nm^3.

Further analysis of the PBDE congener pattern revealed that the emission profile was very similar to the percent composition of a Technical mixture of Pentabromodiphenylether as shown in Fig. 4. For this analysis, the concentrations of the 10 most abundant PBDE congeners found in sinter plant emissions (See Table 3) were normalised and compared with the weight concentrations of these PBDEs in a commercially available Pentabromodiphenyl Oxide Technical mixture for which the exact chemical composition was available (Great Lakes DE-71, Technical Mixture, Wellington Laboratories). As depicted in Fig. 4, a good agreement between the congener pattern observed in sinter plant emissions and the congener pattern of the Pentabromodiphenyl Oxide technical mixture was observed.

The only previous noteworthy study describing emissions of PBDEs from the iron ore sintering process was carried out by Wang et al. (2010) for several sinter plants in Taiwan. In this research, the congener profiles reported showed a very clear predominance of highly brominated-substituted congeners, namely BDE-209, -208, -207, -206, and -183. As a result, it was difficult to directly compare the results of both studies since these PBDEs were not analysed in this study. However it was noted that with regard to the low- to medium - brominated congeners, BDE-47 and BDE-99 were predominant in the sinter plants investigated in Taiwan which was in good agreement with the results obtained at UK sinter plants. At this stage, it is difficult to explain why the congener profiles observed from UK plants would exhibit a pattern similar to the composition of a Pentabromodiphenylether technical mixture; however it would appear highly unlikely that if PBDEs were formed in the process, such a distinctive profile would be obtained. Accordingly, work was carried out to characterise further the PBDE chemical composition of input materials (raw sinter mix, iron ores, fuels) entering the sinter plant to determine whether the materials used in sintering could contain PBDEs prior thermal treatment.

4.3 Raw Material Input / Output Analysis – Mass Balances of PBDEs

In order to study in more detail the distribution of PBDEs in the iron ore sintering process, representative samples of input materials (raw sinter mix) and output materials (sinter product, waste dusts from the electrostatic precipitators: ESP) were collected and analysed for their PBDE content for a total of four beds of materials processed at Sinter Plant A (Bed #s 2258, 2259, 2265, and 2272). The analytical results were used to carry out mass balance calculations of PBDE input / outputs in the iron ore sintering process. For input calculations, PBDE concentrations in the raw sinter mix were multiplied by the bed tonnage and divided by the sinter production. With regard to the sinter product, PBDE outputs were calculated using the PBDE concentrations in the sinter product and by taking into account the sinter production. The amount of ESP dust generated per bed of material is not usually measured accurately; however the amounts produced were estimated assuming that the particulate emission concentration at the inlet of the ESP was 850 mg/Nm^3 and that the efficiency of the ESP was 94% (reducing the particulate emissions down to 50 mg/Nm^3). By multiplying the amount of dust theoretically captured by the ESP with the stack flow rate and by taking into consideration the bed processing time, it was possible to estimate the amounts of waste ESP dusts produced per sinter bed. For Sinter Plant A, the amount of dust produced was estimated

to be 1.5 kg/ton sinter produced. PBDE outputs were calculated using this figure and the sinter production for each bed of material investigated. Finally, stack emission outputs were estimated using the mean concentrations determined in this study (Table 3) which was multiplied by the stack emission flow rate and divided by the sinter production. The detailed results of the calculations are provided as supplementary information (Table SI-1). However, to simplify the data, Table 4 summarises the PBDE inputs and outputs expressed in mg/tonne sinter for each bed of material investigated and the percent distribution of PBDE found in output materials after thermal processing. This facilitated estimation the proportion of PBDEs actually destroyed during sintering.

Analysis of the results revealed that PBDEs were already present in the raw sinter mix in significant amounts before thermal treatment in the process and were originating from the raw materials. This result was relatively unexpected as no previous studies highlighted the presence of PBDEs in the raw materials used in the sintering process. PBDEs were also found in waste ESP dusts in relatively high concentrations and in the sinter product at low concentrations. The results for individual and the sum of the 9 most abundant PBDE congeners are reported in Table SI-1 (Supplementary information). With regard to the raw sinter mix, total PBDE concentrations ranged from 11 to 22 μg/kg, while the range of concentrations observed in the sinter product was much lower (ca. 0.5 to 2.2 μg/kg). The highest concentrations of PBDEs were found in the ESP dusts ranging from 22 to 81 μg/kg. In terms of input, between 13 and 26 mg/ton sinter of PBDEs were found in the raw sinter mix (Table 4). In contrast, very low PBDE output figures were found in the sinter product, ESP dusts and stack emissions (ca. < 2 mg/ton sinter). Stack PBDE outputs represented only less than 4% of PBDE inputs. Overall, the results showed that between 80% and 95% of PBDEs entering the sintering process via the raw materials were destroyed during thermal treatment (Table 4).

To understand further the source of PBDEs in input raw materials, several types of raw materials were selected and analysed for their PBDE (sum of seven congeners) content. These materials are typically mixed together in a bed to constitute the raw sinter mix. These consisted of a series of 26 iron ores typically used at Tata Steel sinter plants, 20 revert materials which included recycled materials from other processes in the integrated steelworks (i.e. blast furnaces, steelmaking plant, rolling mills), 3 fuel samples (i.e. coke breeze) and flux samples such as limestone and olivine. The mean PBDE and range of concentrations observed are summarised in Table 5.

PBDEs were mostly found in iron ores (ca. 992 ng/kg), revert materials (ca. 8286 ng/kg) and fuels (ca. 4891 ng/kg). For most types of material, a relatively wide range of concentrations was observed showing a high variability in the PBDE content of the materials used in the iron ore sintering process. When comparing the iron ore ∑PBDE concentrations (5 - 1623 ng/kg) to those reported for soil samples at several locations such as Spain (Eljarrat et al., 2008), China (Chen et al., 2012), USA (Yun et al., 2008) and Sweden (Sellstrom et al., 2005), it was found that the iron ores used in sintering fell within the range of concentrations reported previously for soils (140 - 260000 ng/kg). The same was observed for the fuels used in sintering. These results suggested that PBDEs were already present in some input materials to the sintering process and were thus perhaps not formed during thermal treatment. The resemblance between the congener pattern in some input materials and that in the Penta-BDE commercial formulation suggests that exposure of input materials to a Penta-BDE source is occurring at some point. This source in the raw materials is currently unknown, although it is assumed that their presence may occur between the mining of iron ore and coals, storage, transportation and preparation for the commercial sintering process. However, with over thirty different sources of iron ores from across the world and a similar situation for coals, it was not feasible to investigate this further in the current study. The revert materials did exhibit higher PBDE concentrations than other types of materials; this result was also difficult to explain. It may be due to the fact that the PBDEs which are transferred to the blast furnaces and downstream processes via the sinter product are volatilised and concentrated further in waste dusts emitted from the blast furnace / steelmaking operations, however further work would be needed to confirm this. The contribution of each type of input materials to the sinter plant was studied in more detail for five different sinter beds, and the results depicted in Fig. 5. As may be seen from Fig. 5, for some beds, the main PBDE inputs were mostly associated with the revert materials (ca. 60 – 80%), but for some other beds PBDEs originated equally from the iron ores, revert and fuels materials (ca. 20 to 40% each). For all beds, PBDE inputs from fluxes (i.e. limestone / olivine) were negligible. These results highlighted the fact that there were multiple raw material sources of PBDEs in the sintering process with significant variability.

The mean PBDE congener profiles for each type of input material was studied and the results depicted in Fig. 6. The congener profiles for each type of the raw materials (iron ores, fuels, reverts and fluxes were almost identical with BDE-47 and BDE-99 representing the majority of ∑PBDE content. The congener profiles in all components appeared to be similar to that of

the PentaBDE commercial formulations (La Guardia et al. 2006), in good agreement with the data described earlier for sinter plant stack emissions.

4.4 Results from the sinter pot study (PBDEs and PBDD/Fs)

A series of sinter pot experiments were carried out to investigate whether PBDEs and PBDD/Fs could be formed in the sintering process following similar pathways to those identified for their chlorinated homologues (PCDD/Fs and PCBs) such as *de novo* synthesis. Experiments were also carried out to investigate whether PBDEs could be potential PBDD/F precursors in the sintering process *via* thermal conversion of PBDEs into PBDD/Fs as shown in laboratory experiments by Buser (1986). To this end, KBr was added at two addition rates (74.5 mg/kg and 225 mg/kg RSM: experiments 2 and 3) to the raw sinter mix, while PBDE technical commercial mixtures of Penta- and Deca-BDE were added at 50 μg/kg RSM in experiment 4. In experiment 5, both KBr (high addition rate) and the two technical PBDE formulations at 50 μg/kg were added. The results obtained in experiments 2 to 5 were compared with a base case for which no KBr or PBDE technical mixture was added to the raw sinter mix (experiment 1). Experiment 1 can be associated with typical operations at a commercial sinter plant. Fig. 7 depicts the PBDE inputs (raw sinter mix) and outputs (sinter product + emissions) expressed as ng/kg raw sinter mix for each experiment. Fig. 8 shows the PBDD/F emissions expressed in ng WHO-TEQ PBDD/F/kg raw sinter mix.

Analysis of the PBDE data showed that in experiments 1 to 3, for which no PBDEs were added, there was a mean overall ∑PBDE input of 1400 ng/kg raw sinter mix (range: 1400-2100 ng/kg raw sinter mix respectively). In experiments 4 and 5, where PBDE technical formulations were added, PBDE concentrations were 18000 and 19000 ng/kg raw sinter mix respectively highlighting the additional PBDE inputs (Fig. 7). However, examination of PBDE outputs showed that in all experiments there was net destruction of ∑PBDEs with an average of 88% (range: 79-96%). This result was consistent with the mass balance data previously described in Section 1.4.3. The addition of KBr in experiments 2 and 3 did not result in any significant increase in ∑PBDE outputs with net PBDE reductions of 90% and 79%, respectively. This result suggested that *de novo* synthesis of PBDEs did not occur in the sintering process, rather destruction of PBDEs that were already present in the raw materials prior to thermal treatment.

Examination of the PBDD/F results (Fig. 8) showed that very low PBDD/F emissions were observed in experiment 1 where no KBr was added to the raw sinter mix. However, the

results obtained for experiments 2 and 3 showed a marked increase in PBDD/F emissions with increasing availability of bromide. These results suggest that PBDD/F formation in iron ore sintering could follow a similar pathway to that of their chlorinated homologues (i.e. *de novo* formation). It must be noted however that the relatively high addition rates of bromide used in this study were not representative of standard operating conditions for a commercial sinter plant for which bromide concentrations are typically below 5 mg/kg. These high addition rates of bromide were only used for research purposes to study a possible link between bromide concentrations in the raw sinter mix and PBDD/F sinter plant emissions. Interestingly, no significant increase in PBDD/F emissions was observed in experiment 4 where significant additions of Penta-BDE and Deca-BDE technical mixtures were used. This result suggests that PBDD/Fs were not formed *via* the conversion of PBDEs used as precursors in iron ore sintering. In all sinter pot experiments, PBDFs constituted the majority of PBDD/F emissions. On average, 89 % (range: 55-98%) of ∑PBDD/Fs were PBDFs with 2,3,7,8-TBDF the dominant congener in 7 out of 10 sinter pot runs as previously observed in the emissions of the full scale sinter plant (Table 2).

5. Conclusions

This study showed that both PBDEs and PBDD/Fs were emitted from the iron ore sintering process. With regard to PBDD/Fs, the mean emission concentrations were 0.14 ng WHO-TEQ/m^3 assuming that PBDD/F and PCDD/F have identical toxic equivalency factors (WHO-TEFs). This study showed that PBDD/F emissions were significantly lower than those of PCDD/Fs in the same samples, accounting for only ca. 10% of the total WHO-TEQ emission concentrations (PBDD/Fs + PCDD/Fs). The average concentration in sinter plant emissions of the sum of 36 PBDE congeners was 295 ng/Nm^3 with a standard deviation of 96 ng/Nm^3. The PBDE congener pattern was very similar to that of a Penta-BDE formulation. PBDE mass balances were carried out at a full scale sinter plant showing that PBDEs were already present in the raw materials such as iron ores and coke breeze and that a significant proportion of the PBDE inputs were actually destroyed during the process (ca. 80 to 95%). While detailed source attribution of the PBDEs in the raw materials was outside the scope of this study, the similarity of the congener pattern in some raw materials to the Penta-BDE formulation, suggests that contamination of such raw materials occurred prior to sintering. Laboratory tests using an experimental sinter pot were carried out to study the formation mechanisms of PBDD/Fs and PBDEs. Results showed that PBDD/F formation increased with increasing amounts of bromide in the raw sinter mix indicating a possible *de novo* formation

pathway. However, this was not the case for PBDEs for which the bromide content of the raw mix exerted no influence. In fact, the results suggested that PBDEs are not formed in iron ore sintering, but instead the PBDEs present in the raw materials are destroyed. Finally, the sinter pot tests showed that PBDD/F formation was not influenced by the presence of PBDEs in the raw sinter mix. This suggests that PBDEs do not act as PBDD/F precursors during sintering.

6. References

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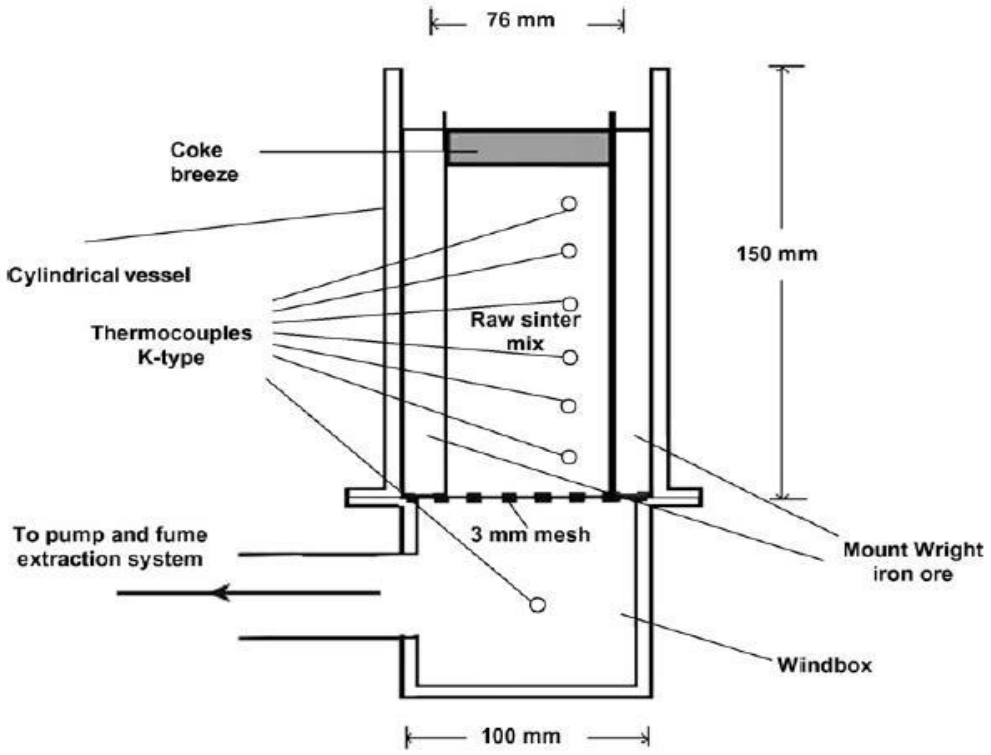


***Figure 1 – A schematic diagram of the laboratory sinter pot apparatus used to investigate the potential formation of PBDEs and PBDD/Fs in iron ore sintering* (Ooi et al., 2008)**

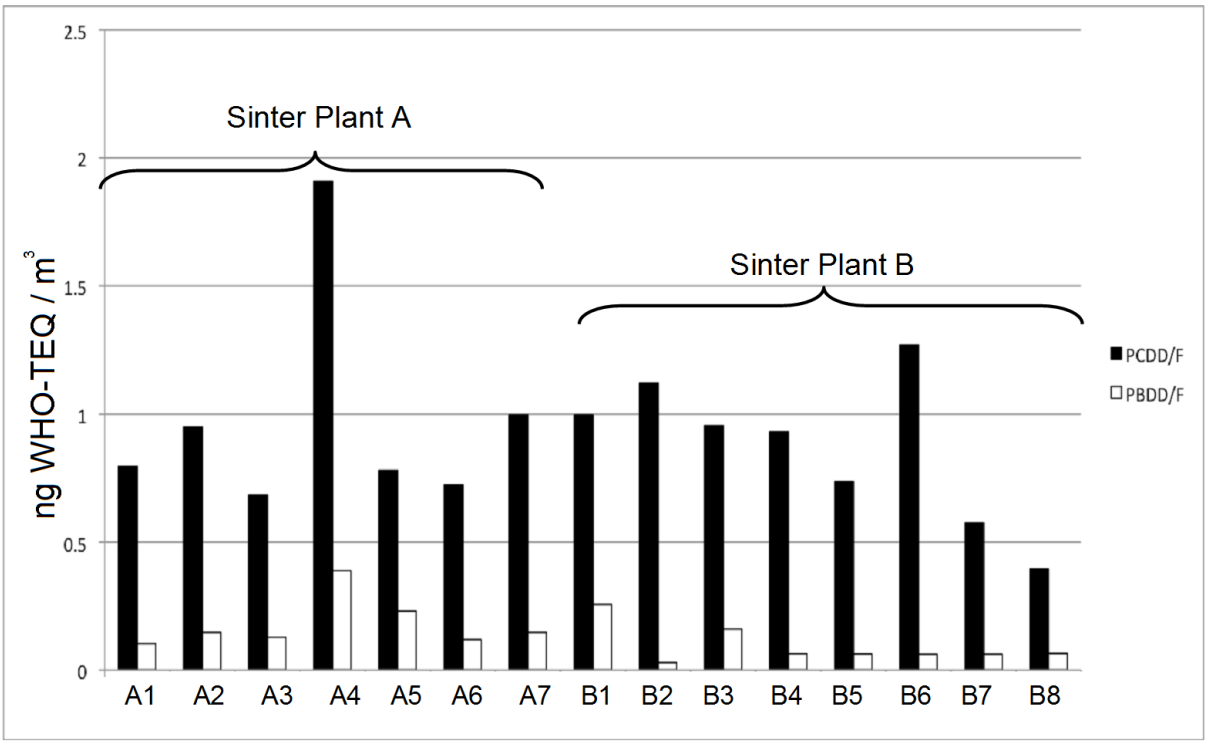
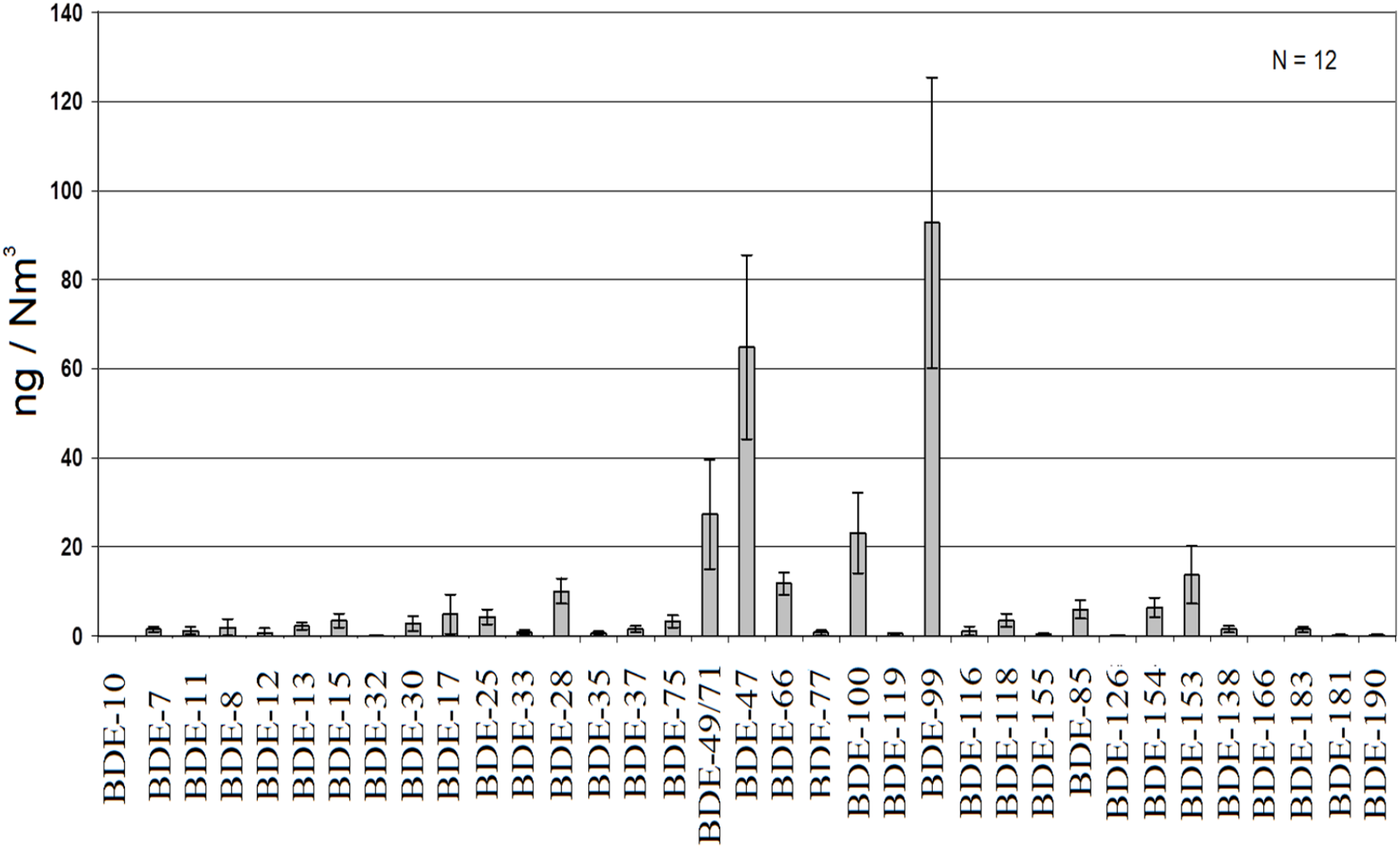


Figure 2 - PCDD/F and PBDD/F WHO-TEQ concentrations at two UK sinter plants operated by Tata Steel.



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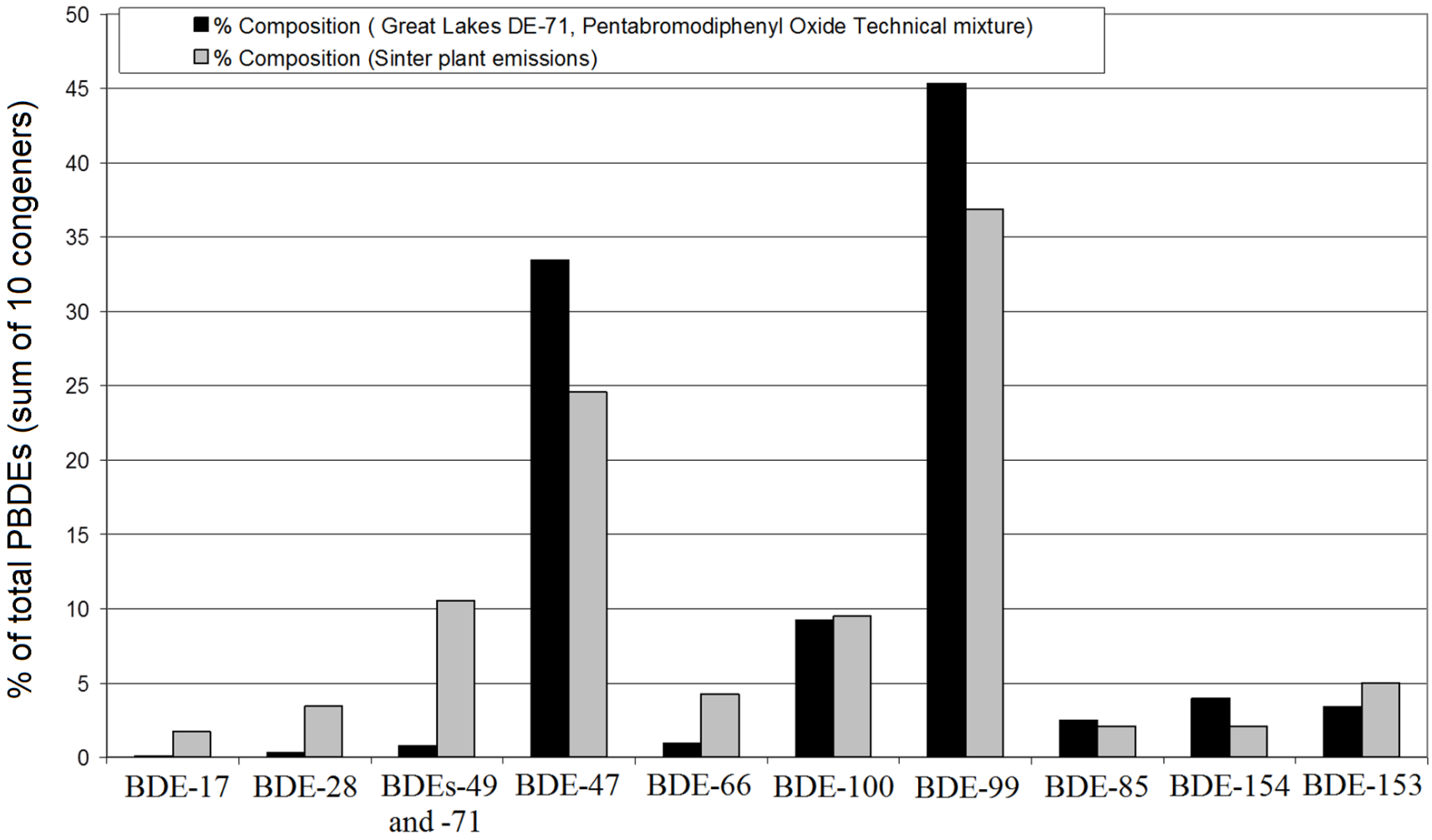
674 ***Fig. 3 – PBDE emission concentrations and congener profile at a UK sinter plant operated by Tata Steel***



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676 ***Fig. 4. Comparison between the percent composition of PBDEs in a Pentabromodiphenyl Oxide mixture and the percent composition of***

677 ***PBDEs in sinter plant emissions.***

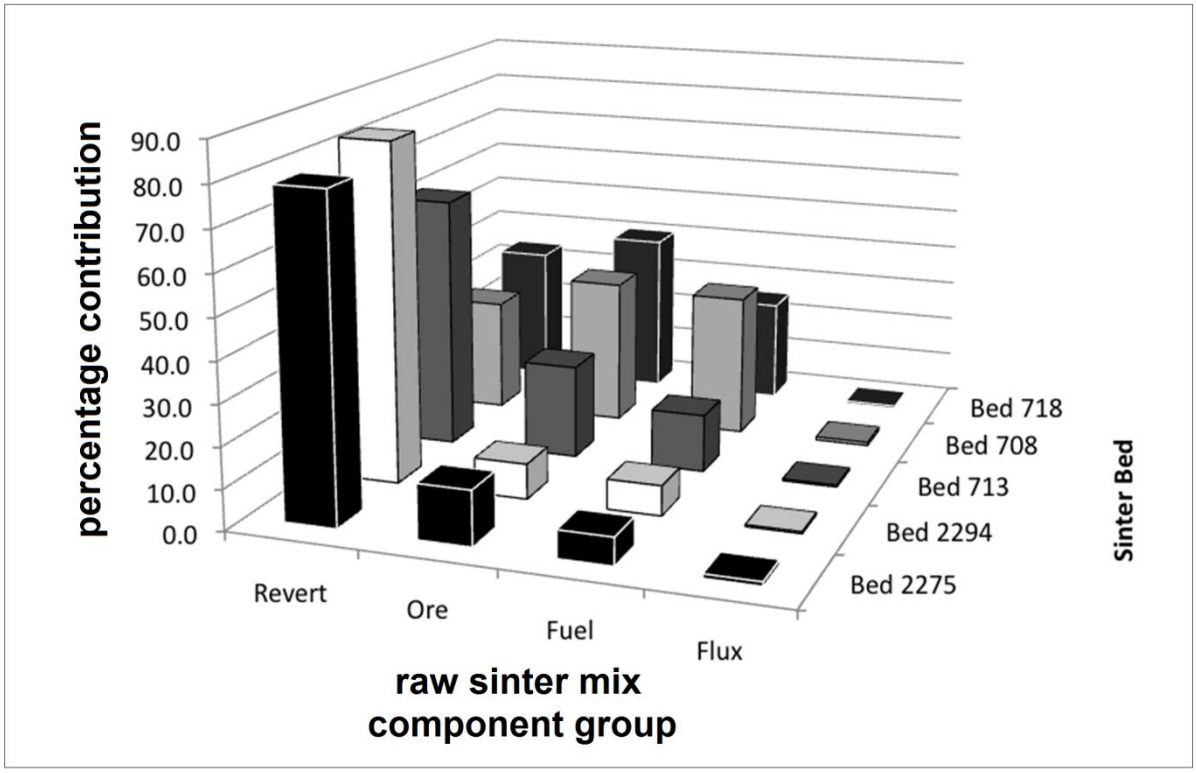

Fig. 5 – Contribution of each component of the raw sinter mix to total PBDE inputs.

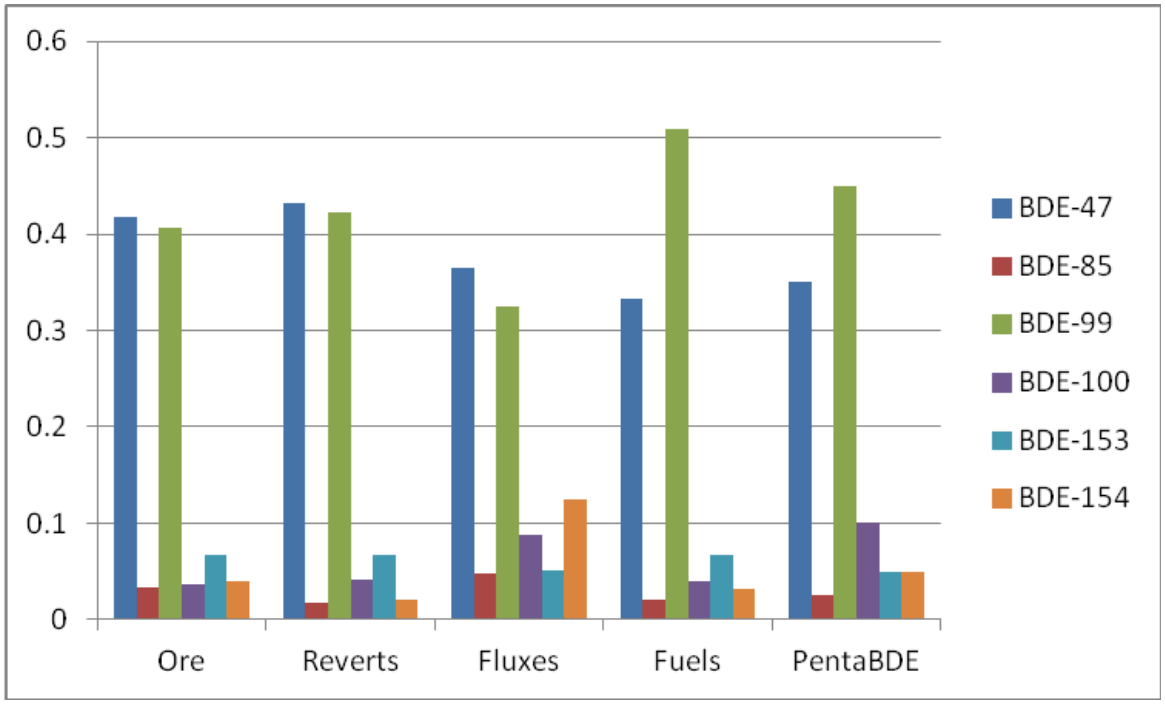

Fig. 6 – Average congener profiles for RSM component groups and the PentaBDE mixture DE-71 (La Guardia et al. 2006).

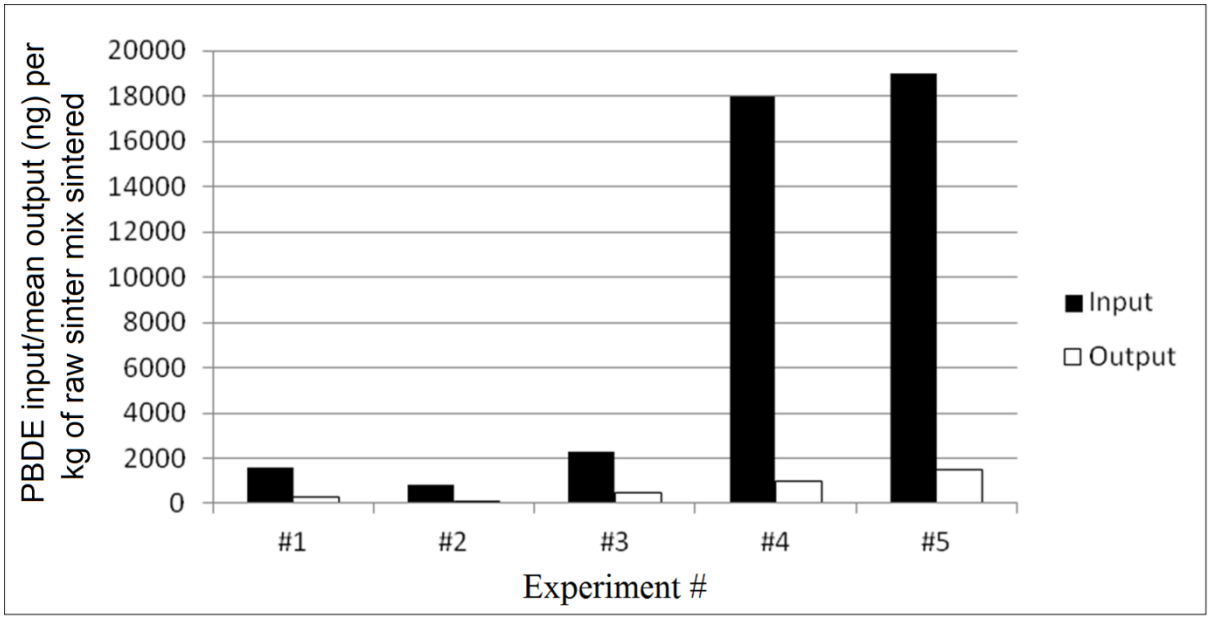

Fig. 7: Input and outputs of ∑PBDEs (ng) per kg of raw sinter mix for each laboratory sinter pot experiment carried out to investigate the possible formation of PBDEs in iron ore sintering

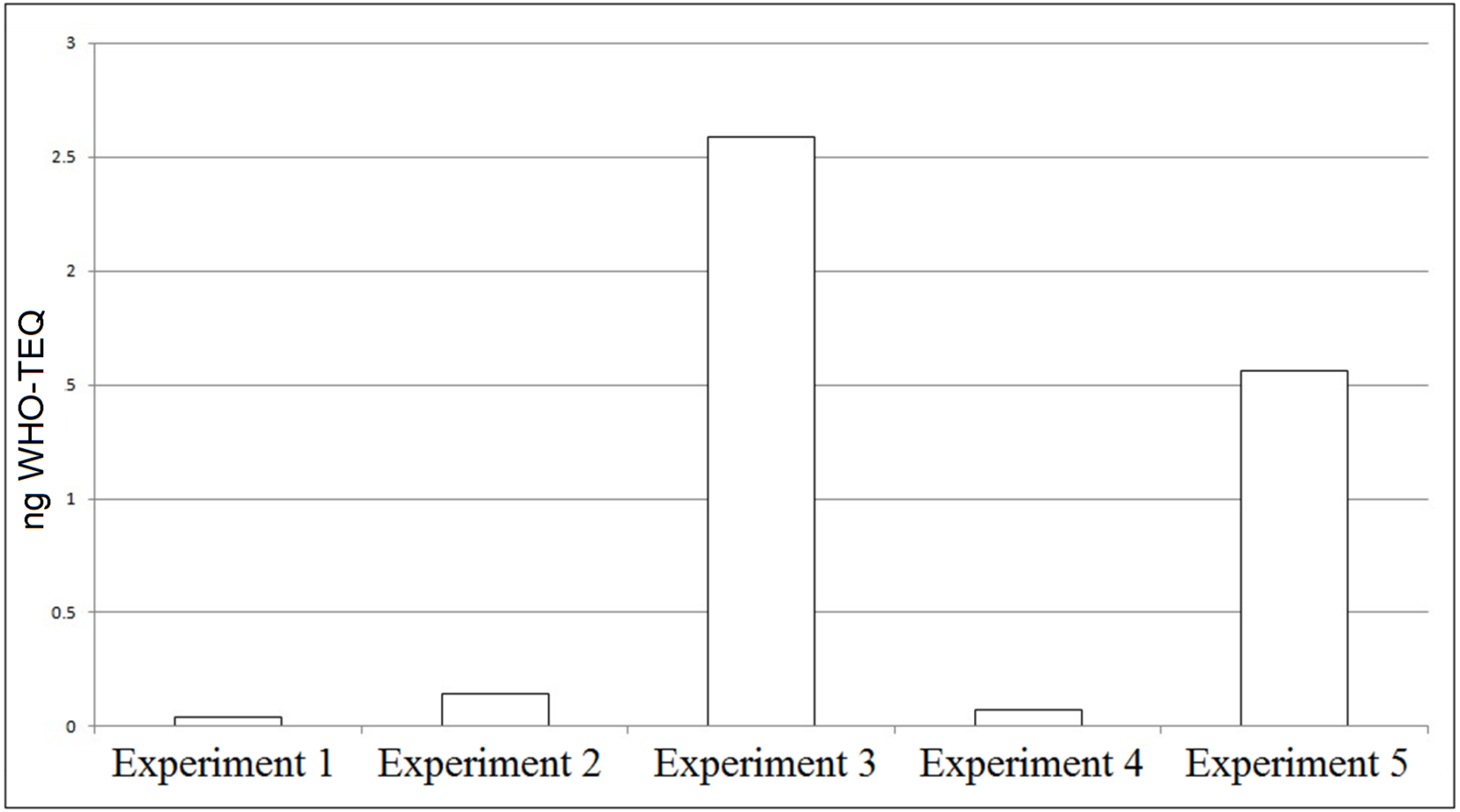

Fig. 8: Emissions of PBDD/Fs expressed as ng-WHO-TEQ formed per kg of raw sinter mix for each laboratory sinter pot experiment carried out to investigate the possible formation of PBDD/Fs in iron ore sintering

Table 1 – Laboratory Sinter Pot Experimental Conditions to study PBDE and PBDD/F formation in the iron ore sintering process

Experiment N.	Condition
1	"Base Case" (Standard Raw Sinter Mix : RSM)
2	"Base Case"+ 74.5 mg/kg KBr (50 mg/kg Br^-)
3	"Base Case" + 224 mg/kg KBr (150 mg/kg Br^-)
4	"Base Case" + PBDE Penta- and Octa- technical mixtures [a]
5	"Base Case" + 224 mg/kg KBr (150 mg/kg Br^-) + PBDE Penta- and Octa-technical mixtures [a]

[a] 50 µg / kg PentaBDE (DE-71) and 50 µg/kg DecaBDE (DE-83) (Cambridge Isotope Laboratories (CIL), Andover, MA, USA)

Table 2. PBDD/F and PCDD/F emission concentrations at two UK sinter plants operated by Tata Steel.

Compound	Sinter Plant B (N = 8) Emission concentrations (ng/Nm^3)		Sinter Plant A (N = 7) Emission concentrations (ng/Nm^3)	
PBDD/Fs	**Mean**	**Range**	**Mean**	**Range**
2378-TBDF	0.12	0.04 - 0.28	0.26	0.14 - 0.57
12378-PeBDF	0.12	0.05 - 0.38	0.21	0.14 - 0.39
23478-PeBDF	0.11	0.04 - 0.31	0.19	0.12 - 0.34
123478-HxBDF	< 0.003[a]	< 0.003 [a]	< 0.003 [a]	< 0.003
∑ PBDFs	0.35	0.12 - 0.97	0.66	0.42 - 1.30
2378-TBDD	0.02	0.01 - 0.04	0.05	0.01 - 0.12
12378-PeBDD	0.01	< 0.003 - 0.005	0.01	0.007 - 0.02
123478/123678-HxBDD	< 0.003 [a]	< 0.003 [a]	0.01	< 0.002 - 0.02
123789-HxBDD	< 0.003 [a]	< 0.003 [a]	0.006	< 0.003 - 0.006
∑ PBDDs	0.02	0.005 - 0.06	0.05	0.02 - 0.13
WHO-TEQ (PBDD/Fs)	0.10	0.03 - 0.26	0.18	0.10 - 0.39
PCDD/Fs				
WHO-TEQ (PCDD/Fs)	1.01	0.46 – 1.50	1.17	0.80 – 2.40

[a] Compound was not detected. The value indicated is the limit of detection.

Table 3. PBDE concentrations (ng/Nm^3) of the 10 most abundant PBDEs and the sum of 36 PBDE congeners in emissions from a sinter plant in the UK operated by Tata Steel.

Compound	Emission concentrations N = 12 measurements	
	Mean	Standard deviation
BDE-17 (2,2',4-TrBDE)	4.9	4.4
BDE-28 (2,4,4'-TrBDE)	10.1	2.8
BDE-49 and BDE-71[a] (2,2',4,5' & 2,3',4',6-TeBDE)	27.3	12.2
BDE-47 (2,2',4,4'-TeBDE)	64.9	20.6
BDE-66 (2,3',4,4'-TeBDE)	11.8	2.5
BDE-100 (2,2',4,4',6-PeBDE)	23.1	9.0
BDE-99 (2,2',4,4',5-PeBDE)	92.8	32.6
BDE-85 (2,2',3,4,4'-PeBDE)	6.0	2.1
BDE-154 (2,2',4,4',5,6'-HxBDE)	6.5	2.2
BDE-153 (2,2',4,4',5,5'-HxBDE)	13.7	6.5
Σ PBDEs (36 congeners)	295	96

[a] Compounds co-eluted.

Table 4. PBDE inputs / outputs and distribution at an iron ore sintering plant operated by Tata Steel. The results are expressed in mg / ton sinter produced for four beds of materials.

	PBDE inputs / outputs expressed in mg / ton sinter				PBDE distribution in the iron ore sintering process (%)			
	Raw mix	Sinter product	ESP dusts	Stack emissions	ESP dusts	Sinter product	Stack emissions	Destroyed during sintering
Bed 2258	26.0	0.5	0.06	0.7	0.2	1.9	2.7	95.2
Bed 2259	13.5	2.2	0.06	0.5	0.4	16.0	3.7	79.9
Bed 2265	15.1	0.6	0.05	0.6	0.3	4.0	4.0	91.7
Bed 2272	14.5	1.2	0.20	0.6	1.4	8.3	4.1	86.2

Table 5. Average and range of concentrations (ng/kg) for PBDEs[a] in the components of raw sinter mix used in the iron ore sintering process.

Component	n	Mean	Range
Iron Ores	26	992	5 – 1623
Reverts	20	8286	30 – 11263
Fuels	3	4891	2092 – 8133
Fluxes	5	240	9 – 940

[a]Sum of seven PBDE congeners (BDE-47; BDE-85; BDE-99; BDE-100; BDE-153; BDE154 ; BDE-183).

Supplementary information

Table SI-1. Detailed PBDE mass balances at an iron ore sintering plant operated by Tata Steel in the UK for four beds of materials

Sinter Bed Conditions	Bed 2258	Bed 2259	Bed 2265	Bed 2272
Raw Sinter Mix (Tonnes)	60378	60097	60867	60776
Sinter production (Tonnes)	50440	49316	52608	52324
Estimated waste ESP dust produced (Tonnes)	126	123	132	131
Bed duration (h)	111.5	86	96.5	105.3
Stack flow rate (Nm^3/s)	348	348	348	348
Material PBDE input concentrations (µg/kg)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.15	0.07	0.08	0.021
BDE-28	0.39	0.19	0.23	0.18
BDE-49	2.0	0.9	1.1	0.9
BDE-47	3.8	1.9	2.3	2.3
BDE-85	1.0	0.6	0.5	0.7
BDE-100	1.4	0.8	0.2	0.7
BDE-99	10.0	5.1	6.5	5.6
BDE-153	2.6	1.3	1.7	1.4
BDE-154	0.5	0.3	0.4	0.6
Σ PBDEs (9 congeners)	21.8	11.1	13.0	12.5
Inputs to Sinter Plant (expressed in g)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	9.1	4.1	5.1	1.3
BDE-28	23.5	11.4	14.0	10.9
BDE-49	120.8	56.5	67.0	57.1
BDE-47	229.4	114.2	140.0	139.8
BDE-85	60.4	34.3	32.9	43.2
BDE-100	84.5	45.7	12.2	43.2

BDE-99	603.8	306.5	395.6	340.3
BDE-153	157.0	78.1	103.5	85.1
BDE-154	30.2	16.2	23.7	37.7
Σ PBDEs (9 congeners)	1318.7	667.0	793.9	758.5
Output to sinter product (µg / kg)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.002	0.020	0.006	<0.002
BDE-28	0.004	0.027	0.008	0.024
BDE-49	0.014	0.054	0.016	0.260
BDE-47	0.078	0.760	0.190	0.270
BDE-85	0.160	0.160	0.013	0.250
BDE-100	0.130	0.260	0.130	<0.005
BDE-99	0.130	0.310	0.080	0.086
BDE-153	<0.01	0.270	0.083	0.240
BDE-154	<0.01	0.300	0.053	0.093
Σ PBDEs (9 congeners)	0.520	2.200	0.580	1.200
Output to sinter product (g)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.08	0.99	0.32	n/a
BDE-28	0.19	1.33	0.41	1.26
BDE-49	0.71	2.66	0.84	13.60
BDE-47	3.93	37.48	10.00	14.13
BDE-85	8.07	7.89	0.68	13.08
BDE-100	6.55	12.8	6.8	n/a
BDE-99	6.55	15.3	4.2	4.5
BDE-153	n/a	13.3	4.4	12.6
BDE-154	n/a	14.8	2.8	4.9
Σ PBDEs (9 congeners)	26.0	108.5	30.5	62.8

Output to waste ESP dust (µg / kg)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.089	0.078	0.12	0.16
BDE-28	0.25	0.25	0.3	0.57
BDE-49	1.3	1.4	1.5	3.6
BDE-47	2.4	2.5	2.7	7.9
BDE-85	0.8	1.0	0.82	4.1
BDE-100	1.6	1.7	1.3	4.1
BDE-99	9.3	11.0	7.7	39.0
BDE-153	5.3	4.9	4.3	17.5
BDE-154	1.1	1.2	1.0	3.8
Σ PBDEs (9 congeners)	22.2	24.0	19.8	80.8
Output to waste ESP dust (g)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.01	0.01	0.02	0.02
BDE-28	0.03	0.03	0.04	0.08
BDE-49	0.16	0.17	0.20	0.47
BDE-47	0.3	0.31	0.36	1.04
BDE-85	0.11	0.12	0.11	0.54
BDE-100	0.2	0.21	0.17	0.53
BDE-99	1.17	1.36	1.01	5.10
BDE-153	0.67	0.60	0.57	2.29
BDE-154	0.14	0.15	0.13	0.50
Σ PBDEs (9 congeners)	2.8	3.0	2.6	10.6
Output to sinter plant stack (ng/Nm^3)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	4.9	4.9	4.9	4.9
BDE-28	10.1	10.1	10.1	10.1
BDE-49	27.3	27.3	27.3	27.3

BDE-47	64.9	64.9	64.9	64.9
BDE-85	6.0	6.0	6.0	6.0
BDE-100	23.2	23.2	23.2	23.2
BDE-99	92.8	92.8	92.8	92.8
BDE-153	13.7	13.7	13.7	13.7
BDE-154	6.5	6.5	6.5	6.5
Σ PBDEs (9 congeners)	249.4	249.4	249.4	249.4
Output to sinter plant stack (g)	Bed 2258	Bed 2259	Bed 2265	Bed 2272
BDE-17	0.7	0.5	0.6	0.6
BDE-28	1.4	1.1	1.2	1.3
BDE-49	3.8	2.9	3.3	3.6
BDE-47	9.1	7.0	7.8	8.6
BDE-85	0.8	0.6	0.7	0.8
BDE-100	3.2	2.5	2.8	3.1
BDE-99	13.0	10.0	11.2	12.2
BDE-153	1.9	1.5	1.7	1.8
BDE-154	0.9	0.7	0.8	0.9
Σ PBDEs (9 congeners)	34.8	26.9	30.2	32.9